APPENDIX I.

QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

State of California
California Environmental Protection Agency
Air Resources Board

QUALITY ASSURANCE PLAN

FOR PESTICIDE MONITORING

Prepared by the

Monitoring and Laboratory Division

and

Stationary Source Division

Revised: February 4, 1994

APPROVED:

Genevieve Shiroma, Chief
Toxic Air Contaminant
Identification Branch

, Chief
Quality Management and Operations
Support Branch

George Lew, Chief
Engineering Evaluation Branch

This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signifiy that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS

APPENDIX

QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) an application has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, ambient and application are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

A. Quality Assurance Policy Statement

It is the policy of the ARB to provide DPR with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

II. Siting

Probe siting criteria for ambient pesticide monitoring are listed in TABLE 1. Normally four sites will be chosen. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. One of these sites is usually designated to be an urban area "background" site and is located away from any expected applications; however, because application sites are not known prior to the start of monitoring, a "zero level" background may not occur. Detectable levels of some pesticides may also be found at an urban area background site if they are marketed for residential as well as commercial use.

Probe siting criteria for placement of samplers near a pesticide application for collection of samples are the same as ambient monitoring (TABLE 1). In addition, the placement of the application samplers should be to obtain upwind and downwind concentrations of the pesticide. Since winds are variable and do not always conform to expected patterns, the goal is to surround the application field with one sampler on each side (assuming the normal rectangular shape) at a distance of about 20 yards from the perimeter of the field. However, conditions at the site will dictate the actual placement of monitoring stations. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed.

III. Sampling

All sampling will be coordinated through the County Agricultural Commissioner's Office and the local Air Quality Management District (AQMD) or Air Pollution Control District (APCD). Monitoring sites will be arranged through the cooperation of applicators, growers or owners for application monitoring. For selection of ambient sites, ARB staff will work through authorized representatives of private companies or government agencies.

A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for ambient monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site.

B. Schedule

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Field application monitoring will follow the schedule guidelines outlined in TABLE 2.

C. Blanks and Spikes

Field blanks should be included with each batch of samples submitted for analysis. This will usually require one blank for an application monitoring and one blank per week for an ambient monitoring program. Whenever possible, trip spikes should be provided for both ambient and application monitoring. The spiked samples should be stored in the same manner as the samples and returned to the laboratory for analysis.

D. Meteorological Station

Data on wind speed and direction will be collected during application monitoring by use of an on-site meteorological station. If appropriate equipment is available, temperature and humidity data should also be collected and all meteorological data recorded on a data logger. Meteorological data are not collected for ambient monitoring.

E. Collocation

For both ambient and application monitoring, precision will be demonstrated by collecting samples from a collocated sampling site. An additional ambient sampler will be collocated with one of the samplers and will be rotated among the sampling sites so that duplicate samples are collected at at least three different sites. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. The duplicate sampler for application monitoring should be downwind at the sampling site where the highest concentrations are expected. When feasible, duplicate application samples should be collected at every site.

F. Calibration

Field flow calibrators (rotometers, flow meters or critical orifices) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard should be verified, certified or calibrated with respect to a primary standard at least once a year with the method clearly documented. Sampling flow rates should be checked in the field and noted before and after each sampling period. Before flow rates are checked, the sampling system should be leak checked.

G. Flow Audit

A flow audit of the field air samplers should be conducted by an independent agency prior to monitoring. If results of this audit indicate actual flow rates differ from the calibrated values by more than 10%, the field calibrators should be rechecked until they meet this objective.

H. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results.

I. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the U.S. EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	1	1	1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270^{o} around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

All samplers should be sited approximately 20 yards from the edge of the field; four samplers to surround the field whenever possible. At least one site should have a collocated (duplicate) sampler.

The approximate sampling schedule for each station is listed below; however, these are only approximate guidelines since starting time and length of application will dictate variances.

- Background sample (minimum 1-hour sample: within 24 hours prior to application).
- Application + 1 hour after application combined sample.
- 2-hour sample from 1 to 3 hours after the application.
- 4-hour sample from 3 to 7 hours after the application.
- 8-hour sample from 7 to 15 hours after the application.
- 9-hour sample from 15 to 24 hours after the application.
- 1st 24-hour sample starting at the end of the 9-hour sample.
- 2nd 24-hour sample starting 24 hours after the end of the 9-hour sample.

IV. Protocol

Prior to conducting any pesticide monitoring, a protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.

2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).

3. Specification of sampling periods and flow rates.

4. Description of the analytical method.

5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

V. Analysis

Analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, an analytical audit and systems audit should be performed by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis. After a history of competence is demonstrated, an audit prior to each analysis is not necessary. However, during each analysis spiked samples should be provided to the laboratory to demonstrate accuracy.

A. Standard Operating Procedures

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. includes: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures. The limit of quantitation must be defined if different than the limit of detection. The method of calculating these values should also be clearly explained in the S.O.P.

1. Instrument and Operating Parameters

   A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

   Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

   The S.O.P. plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Control

   Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection (and quantitation if different from the limit of detection). Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

   The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

   All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as ug/m^3 (microgram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume; however, the minimum and maximum concentrations possible for that sample should also be presented.

The final report should indicate the dates of sampling as well as the dates of analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring are sent to the Department of Pesticide Regulation, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering Evaluation Branch.

A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building). A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum quantitation limit), total number of samples and number of samples above the minimum quantitation limit. For this purpose, collocated samples are averaged and treated as a single sample.

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: ______________ Date: ____/____/____
Sample/Run #: ______________ Time: ______________
Job name: ______________________________
Sample Location: ______________________________
Type of Sample: ______________________________
Log #'s: __________

ACTION	DATE	TIME	INITIALS		METHOD OF STORAGE freezer, ice or dry ice
Sample Collected					
			GIVEN BY	TAKEN BY	
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					

LOG #	ID #	DESCRIPTION

RETURN THIS FORM TO: ______________________________

APPLICATION CHECKLIST

1. Field size.
2. Field location (Section, Range and Township).
3. Application rate.
4. Formulation.
5. Method of application (ground, air, irrigation, injection, tarping after application, etc.)
6. Length of application.
7. Any unusual weather conditions during application or monitoring period (rain, fog, wind).
8. Any visible drift from the field?
9. Pattern of application (e.g., east to west).

APPENDIX II.

SAMPLING PROTOCOL

Don

State of California

MEMORANDUM

To: Genevieve Shiroma, Chief
Toxic Air Contaminant
Identification Branch

Genevieve

Date: July 14, 1993

Subject: Revised Metam Sodium Protocol

From: George Lew, Chief
Engineering Evaluation Branch
Monitoring and Laboratory Division
Air Resources Board

George

Attached is the revised protocol for the MITC monitoring planned for this summer. It covers the ambient monitoring as well as the soil injection application monitoring. The appendices have been omitted because of their length and the fact that all concerned parties should have copies of them from the original protocol.

If you or your staff have questions or need further information, please contact me at 445-0657 or Don Fitzell at 327-0899.

Attachment

cc: Alice Westerinen
Mike Poore

State of California

AIR RESOURCES BOARD

REVISED PESTICIDE MONITORING PROTOCOL

Sampling Procedures for the Monitoring of Certain Breakdown Products of Metam Sodium in Kern County during the Summer of 1993

Engineering Evaluation Branch

Monitoring and Laboratory Division

Project No. C92-070 (Ambient)
C92-070B (Application)

Date: July 14, 1993

APPROVED:

_______________, Project Engineer
Testing Section

_______________, Manager
Testing Section

_______________, Chief
Engineering Evaluation Branch

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Sampling Procedures for the Monitoring of Certain Breakdown Products of Metam Sodium in Kern County during the Summer of 1993

I. Introduction

The Cal/EPA Office of Environmental Health Hazard Assessment (OEHHA) and the Department of Pesticide Regulation (DPR) have requested that the Air Resources Board (ARB) conduct ambient air monitoring for methyl isothiocyanate (MITC). MITC is the primary breakdown product of metam sodium (sodium-N-methyldithiocarbamate). MITC is responsible for the pesticidal activity of metam sodium. In response to this request, ARB staff will conduct a 3-day source impacted ambient monitoring program after an application of metam sodium by soil injection, as well as an ambient monitoring program within populated areas. This monitoring will focus primarily on MITC, although limited monitoring for two other breakdown products, hydrogen sulfide and carbon disulfide may also be conducted.

An extensive Quality Assurance/Quality Control (QA/QC) program was completed (Attachment A) to ensure the accuracy of the results. Because of the emergency nature of the Dunsmuir spill where a railroad car of metam sodium was spilled into the upper Sacramento River, it was not possible to implement full QA/QC procedures at that time. It is felt this thorough QA/QC program substantiates both studies. A monitoring program for MITC was conducted in Brentwood, CA during March of 1993 in order to verify the accuracy of the analytical method as well as have comparison data for the proposed summer application monitoring.

Metam sodium is an herbicide, fungicide, insecticide and nematicide primarily used as a preplant fumigant. Its peak use in California is in Kern County during the months of July and August. Since metam sodium is used in various parts of the state, the monitoring location will be selected by ARB, DPR, OEHHA after identifying those areas with the peak metam sodium usage rate. DPR's "Monitoring Recommendation for Metam-sodium" is presented in Attachment B. Metam sodium is applied by soil injection or sprinkler irrigation. Results of the monitoring will be evaluated by staff of the OEHHA and the DPR.

II. Sampling

A sketch of the sampling apparatus is shown in Attachment C. The apparatus consists of a charcoal adsorbent tube, rain and light cover, rotometer, sampling train support and vacuum pump. Charcoal adsorbent tubes will be used for the collection of MITC and carbon disulfide samples.

Hydrogen sulfide will also be monitored on site using a Jerome portable analyzer. This instrument measures hydrogen sulfide based upon its reaction with a gold film. The Jerome is hand-held and battery operated instrument capable of only providing instantaneous readings at one location. All results are real time and cannot be time averaged. This instrument has a detection limit of 3.0 ppb. Hydrogen sulfide levels will be determined during the application monitoring and also the ambient monitoring, if feasible.

A. Application Monitoring

Air sampling will be coordinated with the appropriate County Office of the Agricultural Commissioner, and an applicator. Four samplers will be set up: one on each side of the field at a distance of about 20 yards. Prior to application, background samples will be taken to establish if any MITC is detectable. A meteorological station will also be set up to determine wind speed and direction. This station will continue to operate throughout the sampling period. A log book will be kept with information on the field size, application rate, formulation, length of application and any other pertinent information.

Ambient air will be pulled through the sampling tubes at a flow rate of approximately 2 liters per minute using battery powered pumps. Duplicate samples will be collected from each sampler for quality assurance purposes. The sampling schedule outlined in ARB's "Quality Assurance Plan for Pesticide Monitoring" (Attachment D) will be followed as closely as practical. Based on the laboratory detection limit of 0.075 ug/sample, the detection limits will range (approximately) from 0.63 ug/m^3 for the one hour background sample to 0.026 ug/m^3 for the 24-hour samples.

B. Ambient Monitoring

Three to five samplers will be set up at various locations throughout the County. Sampling sites will be selected based upon criteria outlined in the "Quality Assurance Plan for Pesticide Monitoring" and will be in population centers near application sites. The samplers will be powered by 115VAC vacuum pumps.

Twenty-four hour samples will be taken Monday through Friday at a flow rate of approximately 2 liters/ minute. Based on the laboratory detection limit of 0.075 ug/sample, the detection limit for the ambient samples will be (approximately) 0.026 ug/m^3. Meteorological data will be obtained for the area of the monitoring, during the period of monitoring, from the California Irrigation Management Information System (CIMIS).

III. Analysis

All samples will be stored in an ice chest containing dry ice or a freezer until analysis. Analysis of MITC samples will be performed by the Department of Health Services Air and Industrial Hygiene Laboratory. The analytical method is extraction with carbon disulfide, separation by gas chromatography using a DB-624 column and measurement by a nitrogen/phosphorus detector. The analytical procedure is described in Attachment E and Attachment F.

At this time it is anticipated that some of the duplicate samples from both the ambient and the application monitoring will be sent to Zeneca (formerly ICI, formerly Stauffer) for carbon disulfide analysis. Detection limit for this compound is 0.3 ppm. A copy of Zeneca's analytical procedure for carbon disulfide can be found in Attachment G.

IV. Quality Assurance

Calibrated rotometers will be used to control sample flow rates. Sampler flow rates will be calibrated prior to and after sampling in the field. Samplers will be leak checked with the sampling media installed prior to and after each sampling period. A field log book will be used to record sample start and stop times, duration of the application, sample IDs, any change in the flow rates, and other pertinent information. A chain of custody sheet will accompany all samples.

The dependent parameters (reproducibility, linearity and minimum detection limit) of the analytical instrument will be checked prior to analysis. A laboratory audit will be conducted prior to sampling in order to review methods and establish the accuracy of the methods through the use of spiked samples. This audit program will be developed by the ARB, DPR, and laboratory staff. Blank sampling tubes will accompany each batch of samples from the field to the lab prior to analysis. Trip spikes will also be prepared by AIHL.

Method development procedures to document the performance of the sampling/ analytical methodology were previously conducted. Methods development data are presented in Attachment F.

V. Personnel

ARB Monitoring personnel will consist of Don Fitzell (Project Engineer) and Jack Rogers and Jack LaBrue (Instrument Technicians).

APPENDIX III.

ANALYTICAL PROCEDURE
EHLB (formerly AIHL)
ICI

AIHL Procedure for the Analysis of MITC

Attn: G. Ruiz

LABORATORY WORKSHEET

Cal/OSHA No. C92-070 Page 1 of 1 LN 30445 et. al

Date Received 11 Aug 93 Instrument Varian Vista GC #6000-348C

Condition of Seals

☐ intact

☑ broken all (sample no.)

☐ absent (sample no.)

Detector Nitrogen - Phosphorus

Carrier Helium 99.999 %

Column: ☑ single ☐ dual cap. ☑

☐ glass ☐ S.S.

length 30 m

phase DB-5 %

film: 1.0 µ i.d. = 0.25 mm

Temperatures (°/C)

injector 200°

detector 300

column: See Below Time (min)

initial

TP (°/min)

final –

Sample Type charcoal in tubes

Flowrates (mL/min):

carrier 30 cm/sec hydrogen 4.5

make up 30 air 175

Electrometer range 12 ATTN

Method in house

Injection Vol (sample/flush) /

Temp. prog: $40^\circ C \xrightarrow[min]{5^\circ C} 70^\circ C \xrightarrow[min]{20^\circ C} 150^\circ C$ Total 10 min

Charcoal desorbed 30 min in 3 mL low benzene CS_2 which had been cooled at least 15 min @ < 0°C freezer after ~~of~~ aliquotting into vial. Kept vials cool before desorption using cold packs in hood in small cardboard box. Charcoal immediately decanted into vial which is ~~then~~ immediately capped & put on Supelco agitator. Immediately re-portioned to 1.8 mL autosampler vials, 2 total, 1 kept for back up in uncontaminated freezer & 1 analyzed within 24 hr of desorption

COLUMN: DB-5, 0.025µ BORE, 1µ FILM THICKNESS, 30m

Chemist Paul Larkin Date 15 Oct 93

Group Leader Date

ICI Procedure for the Analysis Of MITC

METHYL ISOTHIOCYANATE FROM METHAM-SODIUM

DETERMINATION IN AIR

Written by: S. C. Leung

Distribution List

1 - D. J. Brookman
1 - G. L. Cooper
1 - J. A. Kieft
1 - M. G. Kleinschmidt
1 - S. C. Leung
20 - J. C. McKay
1 - W. J. Smith
1 - WRC Central File

de Guigne Technical Center
August 26, 1982
Method No. RRC-82-35

NOTICE

TITLE

METHYL ISOTHIOCYANATE FROM METHAM-SODIUM DETERMINATION IN AIR

I. SCOPE

This method is designed to measure methyl isothiocyanate (MITC) in air. The method is applicable for methyl isothiocyanate concentrations between 0.01 and 6 mg per cubic meter in a 40-liter air sample. Methyl isothiocyanate is the active fumigant to which VAPAM® is converted upon application to soil.

II. SUMMARY OF METHOD

A known volume of air is drawn through a charcoal tube via a battery-operated sampling pump. The methyl isothiocyanate present in the air is quantitatively adsorbed on the charcoal. The charcoal is then desorbed with carbon disulfide; the extract is analyzed for methyl isothiocyanate by gas chromatography with nitrogen-phosphorus alkali flame ionization detection.

III. INTRODUCTION

VAPAM® soil fumigant, common name Metham-sodium, is sodium N-methyldithiocarbamate:

$$\text{Na-S-}\overset{\overset{\Large S}{\|}}{\text{C}}\text{-NH-CH}_3$$

VAPAM® is generally formulated as an aqueous solution containing 32.7% anhydrous sodium salt and is nonvolatile. Its activity is due to decomposition to methyl isothiocyanate (CH_3NCS).

IV. APPARATUS AND REAGENTS

A. Apparatus

1. Gas Chromatograph. Hewlett-Packard Model 5710A or equivalent, equipped with a nitrogen-phosphorus alkali flame ionization detector (NP-AFID).

2. Recorder. Sensitivity of 1 millivolt full scale, 1 second response.

3. Quantitation Aid. Electronic digital integrator, on-line data acquisition system or other device for measuring peak areas.

4. Gas Purification Traps. For purifying helium, air and hydrogen required for gas chromatograph. Model 236 (Guild Corp., P. O. Box 217, Bethel Park, PA 15102) or equivalent.

5. Gas Chromatograph Column. Pyrex tubing (1.8 m x 2 mm i.d.), washed with KOH solution, silanized and dried. Pack the tubing with 10% SP 2250 on 100/120 mesh Supelcoport or equivalent. See Appendix A for details of column preparation and conditioning.

6. Syringe. 10-microliter capacity with fixed needle, Hamilton 701N or equivalent.

7. Personal Air Sampling Pump. DuPont P-200 or equivalent; capable of drawing 100 mL/minute of air through the charcoal tube for 8 hours.

8. Glass Vials. 2-dram, equipped with polyseal-lined caps.

9. Charcoal Tubes. Glass tube with both ends flame sealed, 7 cm long with a 6-mm o.d. and a 4-mm i.d., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. Such charcoal tubes are commercially available from SKC, Inc., Eighty four, PA 15330, Cat. No. 226-01.

10. Charcoal Tube Holder. Nylon sample tube holder equipped with collar clip and tygon connecting tube for supporting the charcoal tube in a vertical position in the employee's breathing zone. SKC Cat. No. 222-3-1, or equivalent.

11. Silica Gel Tubes. For use as moisture pre-trap in the presence of high (>80%) relative humidity. These are glass tubes with both ends flame sealed, 7 cm long with a 6-mm O.D., containing 2 sections of 75/150 mg of silica gel. SKC Cat. No. 226-10, or equivalent.

B. Reagents

1. Carbon Disulfide. Mallinckrodt AR grade, Cat. No. 4352 or equivalent.

2. Gases. Supplied to gas chromatograph via lines equipped with gas purification traps and suitable line regulators.

    a. Helium. High purity cylinder helium.

    b. Hydrogen. High purity cylinder hydrogen.

    c. Air. Dry air, free from organic contaminants, from cylinder or compressor.

3. Methyl Isothiocyanate. Analytical Reagent grade. Aldrich Cat. No. 11777-1.

IV. PROCEDURE

A. Air Sampling

Break both ends of the charcoal tube to provide openings for air to pass through. The smaller section of charcoal is used as a backup section and therefore is placed nearest the sampling pump. Use tubing from the sample tube holder to connect the back of the tube to the pump. Turn on the pump and set the flow rate to 100 mL/min. Calibrate the trap-pump assembly via RRC method 76-46; record the calibration data.

To take an air sample, support the charcoal tube in a vertical position with the sample tube holder and clip the trap to the employee's clothing so that the trap is located as close as possible to his or her breathing zone. Attach the pump to the employee via a convenient pocket. Turn on the pump, and take a 6-8 hour sample. At the end of the sampling period record the time. Remove the trap-pump assembly from the employee; recalibrate the assembly and record the recalibration data.

For sampling at relative humidity greater than 80%, connect a silica gel tube in front of the charcoal tube by means of a short tygon tubing during the entire sampling period. The silica gel is used as a drying agent preceding the charcoal to eliminate the effect of moisture (see Section VI.B.).

B. Gas Chromatographic Conditions

Set the temperature of oven, injection port, and detector on the gas chromatograph. Establish suitable flow rates for the various gases; optimizing the detector response according to the manufacturer's directions.

The following conditions are given for a Hewlett-Packard Model 5710A chromatograph with a N-P AFID detector and a 1.8 m x 2 mm i.d., 10% SP2250 column.

Column temperature:	95°C, isothermal
Injection port temperature:	250°C
Detector temperature:	300°C
Helium carrier gas flow:	30 mL/min
Hydrogen flow:	3 mL/min
Air flow:	60 mL/min
Quantitation:	digital integrator or data system; set attenuation to obtain a measurable peak from 0.5 ng of MITC.

Under the above conditions, MITC elutes in approximately 2.4 minutes.

C. Calibration

Prepare five calibration standards containing 0.1, 1.0, 5.0, 10.0 and 20.0 micrograms of methyl isothiocyanate per mL of carbon disulfide to cover the desired range of calibration. Prepare standard solutions fresh weekly, and refrigerate standard solutions when not in use. Inject 5.0 microliters of each solution into the chromatograph at least twice and record the peak areas. Plot the average peak area against the corresponding MITC concentration (micrograms/mL), and draw the best-fitted straight line through the points. Check calibration periodically by occasionally alternating injections of standards with those of samples.

D. Sample Analysis

Score each charcoal tube with a file in front of the glass wool plug and break the tube open. Remove the glass wool plug and place it in a 2-dram vial that contains 1.0 mL of carbon disulfide. Pour the charcoal in the front section into the vial, tapping the side of the tube to dislodge any charcoal that adheres to the walls. Immediately cap the vial with a polyseal-lined cap. Remove the separating foam plug and transfer the backup section into another 2-dram vial containing 1.0 mL of carbon disulfide; immediately cap the vial. Desorb the MITC for 30 minutes, agitating the sample occasionally to facilitate desorption.

Inject 5.0 microliters of the carbon disulfide extract from each section of the charcoal tube into the gas chromatograph. Dilute the extract if necessary to keep the response(s) within the range. Analyze the sample extracts immediately after calibration has been completed. If analysis of the extract cannot be completed on the same day, refrigerate the extract at 0°C. However, do not store the extract for more than 2 days due to the high volatility of carbon disulfide.

V. CALCULATIONS

A. Mean Flow Rate

Calculate the mean flow rate for the pump-trap assembly by the following equation:

$$F = \text{mean flow rate (L/min)} = \frac{A + B}{2}$$

where A = average initial flow rate, L/min
B = average final flow rate, L/min

B. MITC Concentration in Air

Use the calibration curve and the MITC peak area obtained from the sample extract to determine the amount of MITC in each section of the trap. Calculate the concentration of MITC in air by the following equation:

$$\text{MITC concentration (mg/M}^3\text{)} = \frac{(W1 + W2)}{F \times T}$$

where W1 = weight of MITC found in front section of charcoal tube, micrograms

W2 = weight of MITC found in backup section of charcoal tube, micrograms

F = mean flow rate, L/min
T = sampling time, minutes

VI. DISCUSSION

A. Precision and Accuracy

Desorption Efficiency (DE) for MITC was determined by introduction of known amounts of MITC directly into charcoal tubes at levels of 0.5, 5, 25, and 50 micrograms of MITC. Six replicates were prepared at each of the above levels. All samples were analyzed; the D.E. of MITC is shown in Table 1 (see Reference B for statistical procedure used).

The collection efficiency of this method was tested by generating MITC vapors with the use of the dynamic U-tube system adapted from the literature (References C & D). An average MITC recovery of 94% was obtained for 26 test trials with a relative standard deviation of 10%. Recovery data for MITC in air are shown in Table 2.

The present method was applied also to aqueous solutions of metham-sodium. In this recovery test, a known amount of metham-sodium in aqueous solution was injected onto moistened vermiculite placed at one end of the U-tube while air was pulled through the U-tube at 0.1 L/min and carried the MITC vapors into a charcoal tube at the other end of the U-tube. The presence of water and vermiculite is known to speed up the rate of decomposition of metham-sodium to MITC (Reference E). At the end of each sampling test, both sections of each charcoal tube were removed for desorption and analysis to obtain recovery of MITC. Under these conditions, at least 75% of metham-sodium (up to 190 ug) was converted to MITC in 5 hours. Longer time (16 hours) was required for the conversion of 380 ug of metham-sodium. A summary of the recovery data of MITC from metham-sodium in air is shown in Table 4.

B. Other Comments

The effect of humidity on the recoveries of MITC from air was also studied. A summary of recovery data from air of various relative humidities (R.H.) is shown in Table 5. No significant losses occurred when MITC was sampled at R.H. between 50% and 70%. However, at lower concentrations (less than 0.01 mg/M^3) and R.H. greater than 80%, humidity has a more serious effect (see Table 5). To avoid losses of MITC due to effects of moisture, the use of a silica gel tube preceding the charcoal tube is recommended for sampling at R.H. greater than 80%. Recoveries of MITC at high R.H. (>81%) with the use of the silica gel pre-trap showed no significant differences from recoveries at lower R.H. (see Table 6).

Experimentally no breakthrough was observed when 230 micrograms of MITC was adsorbed in the charcoal tube from air with 70 liters of air pulled through the tube at a sampling flow rate of 200 mL/min. This was determined by analysis of both the front and the backup section of the charcoal tube. In general, if more than 25% of the total sample is in the backup section, significant breakthrough may have occurred and the sample is not valid.

Storage stability tests indicated that recoveries of samples stored for 14 days under refrigeration at 4°C agreed within ±15% relative to those of initial samples (see Table 2).

VII. SAFETY PRECAUTIONS

A. Methyl Isothiocyanate

Methyl isothiocyanate is toxic, skin irritant and lachrymator.

Avoid contact with skin and eye.

Avoid inhalation of mist, sprays or vapors.

Use only with adequate ventilation and wear gloves.

B. Carbon Disulfide

Carbon disulfide is flammable and vapor harmful.

Keep away from heat and open flame.

Keep container closed.

Use only with adequate ventilation.

Avoid prolonged breathing of vapor.

Avoid prolonged or repeated contact with skin.

VIII. REFERENCES

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7411-9 to 36
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7893-7 to 10

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Appendix A

A. Column Preparation and Conditioning

Wash inside of Pyrex column with 1% aqueous KOH and let stand filled with KOH solution 15 minutes. Rinse well with four successive methanol and two successive toluene washes. Fill column with a solution of 5% dimethyldichlorosilane in toluene and let stand 15 minutes. Drain and rinse with toluene. Finally, rinse with methanol and dry with a stream of nitrogen.

Pack the gas chromatographic column with the 10% SP 2250 packing under moderate vacuum with light tapping. Do not use a vibrator. The packing should not extend into the end areas of the column that are heated by the injection port and detector. Install the packed column in the chromatograph with the exit end free. Turn on the carrier gas to 20-40 mL/min, set the initial temperature to 80°C and hold it there for about 30 minutes. This will purge the column of oxygen and water vapor. Increase the column temperature at a rate of 2°C/min. The final conditioning temperature should be 240°C. Condition the column eight hours or more with 20-40 mL/min of carrier gas flowing. After conditioning, cool the oven and complete the installation of the column.

Table 1. Desorption Efficiency (D.E.) of Methyl Isothiocyanate

Test 1			Test 2			Test 3			Test 4		
µg Taken	µg Found	D.E.	µg Taken	µg Found	D.E.	µg Taken	µg Found	D.E.	µg Taken	µg Found	D.E.
0.50	0.42	0.84	5.14	4.71	0.92	21.4	19.8	0.93	51.5	52.3	1.02
0.50	0.43	0.86	5.14	4.93	0.96	21.4	20.1	0.94	51.5	53.0	1.03
0.50	0.43	0.86	5.14	4.86	0.95	21.4	19.8	0.93	51.5	51.4	0.99
0.50	0.43	0.86	5.00	4.60	0.92	21.4	20.4	0.95	51.5	50.6	0.98

n	=	4	4	4	n
Mean D.E.	=	0.86	0.94	0.94	1.01
St. dev.	=	0.010	0.021	0.0096	0.024
CV_1	=	0.012	0.022	0.010	0.024

$$\overline{CV}_1 = 0.018$$

NOTES: CV_1 = coefficient of variation

$\overline{CV}_1$ = Pooled coefficient of variation.

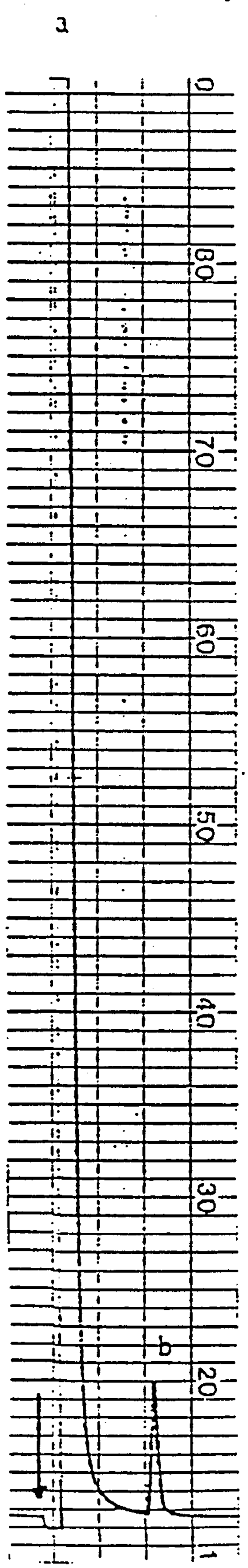
Table 2. Storage Stability of Methyl Isothiocyanate

Test 1			Test 2			Test 3			Test 4		
μg Taken	μg Found	% Recovery	μg Taken	μg Found	% Recovery	μg Taken	μg Found	% Recovery	μg Taken	μg Found	% Recovery
0.50	0.42[a]	84	5.14	4.71[a]	92	21.44	19.8[a]	92	51.45	52.3[a]	102
0.50	0.43[a]	86	5.14	4.93[a]	96	21.44	20.1[a]	94	51.45	53.0[a]	103
0.50	0.43[a]	86	5.14	4.86[a]	95	21.44	19.8[a]	92	51.45	51.1[a]	99
0.50	0.43[a]	86	5.00	4.60[a]	92	21.44	20.4[a]	95	51.45	50.6[a]	98
0.50	0.39[b]	78	5.15	5.16[b]	100	25.47	24.6[b]	97	51.45	50.1[b]	97
0.50	0.39[b]	78	5.15	5.19[b]	101	25.47	24.3[b]	95	51.45	45.3[b]	88
0.50	0.38[c]	76	5.15	4.59[c]	89	25.47	23.2[c]	91	51.45	46.8[c]	91
0.50	0.37[c]	74	5.15	4.71[c]	92	25.47	22.6[c]	89	51.45	55.6[c]	108
0.50	0.38[c]	76	5.14	4.11[c]	80	21.44	15.9[c]	74	51.45	44.9[c]	87
0.50	0.39[c]	78	5.14	4.01c	78	21.44	16.7[c]	78	51.45	45.7c	89

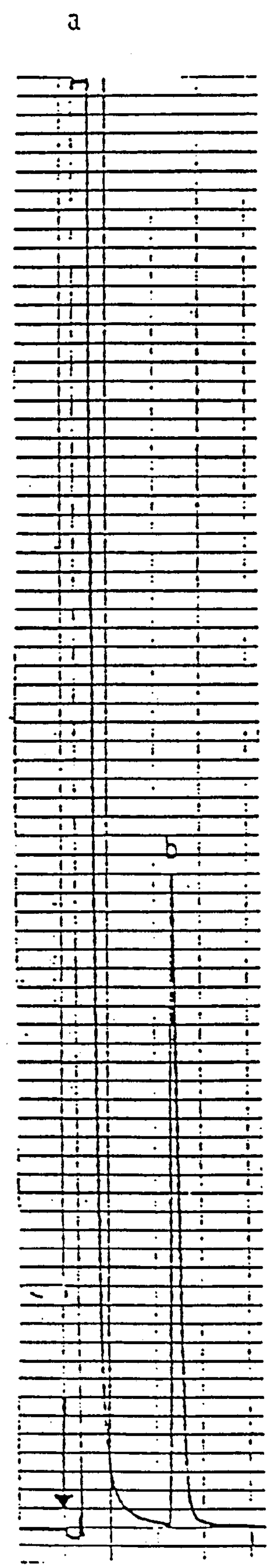
NOTES: a = Samples analyzed after being stored for 1 day under refrigeration
b = Samples analyzed after being stored for 7 days under refrigeration
c = Samples analyzed after being stored for 14 days under refrigeration
% Recovery not corrected for desorption efficiency (D.E.)

FIGURE 1. Typical Chromatogram for MITC Analysis

Standard, 1 ug/mL



Sample 7397-49-8, at 5.1 ug MITC



a = Solvent

b = MITC, 2.3 min.

Table 3. Recovery Data for MITC in Air

Temperature = 65-68°F; R.H. = 58-70%

L/min Flow Rate	Minutes Sampling Time	Liters Air Volume	ug MITC Taken	ug MITC Found	% Recovery
0.1	430	48	0.5	0.44	88
0.1	430	40	0.5	0.44	88
0.1	430	45	0.5	0.44	88
0.1	510	47	0.5	0.36	72
0.1	510	52	0.5	0.37	74
0.1	510	53	0.5	0.39	78
0.1	410	40	5.15	4.20	82
0.1	410	40	5.15	4.49	87
0.1	410	43	5.15	4.72	92
0.1	380	36	5.15	4.71	92
0.1	420	39	5.15	5.34	104
0.1	430	44	5.15	5.05	98
0.1	420	40	10.29	10.9	106
0.1	460	43	25.47	27.3	107
0.1	460	47	25.47	25.7	101
0.1	460	45	25.47	26.0	102
0.1	450	50	25.47	25.3	99
0.1	450	42	25.47	25.2	99
0.1	450	48	25.47	24.2	95
0.1	360	38	51.45	46.9	91
0.1	370	37	51.45	48.6	94
0.1	450	45	51.45	48.5	94
0.1	450	46	51.45	53.4	104
0.1	460	46	51.45	49.5	96
0.1	390	38	51.45	50.6	98
0.1	450	47	227.4	207	91
0.2	370	71	227.4	195	86*
0.2	370	71	225.6	180	80*
0.2	370	66	225.6	179	79*

Mean = 94
RSD = 10%
n = 26

NOTES: % Recovery not corrected for desorption efficiency (D.E.)

* = Samples collected at flow rates greater than 0.1 L/min; not included in the calculation of mean % recovery

Table 4. Recovery Data for MITC from Metham-sodium in Air

L/min Flow Rate	Minute Sampling Time	Liters Air Volume	ug Metham-Sodium Taken	Theoretical ug MITC Taken	ug MITC Found	% MITC Found based on Theoretical MITC Taken
0.11	380	42	23.7	13.4	11.9	89
0.12	400	50	47.0	26.8	25.4	95
0.12	320	38	94.7	53.5	46.3	87
0.12	320	40	189.5	107.2	84.1	79
0.12	430	52	189.5	107.2	79.3	74
0.11	990	110	189.5	107.2	78.7	73
0.11	320	36	379.0	214.0	110	51*
0.11	440	48	379.0	214.0	99	46*
0.13	990	125	379.0	214.0	190	89

NOTES: * = low recoveries on these samples due to incomplete conversion of MITC from Metham-sodium.

Table 5. Effects of Relative Humidity (R.H.) on Recoveries of MITC from Air

Sampling Flow Rate = 0.1 L/min.

% R.H.	No. of Samples	Hours Sampling Time	Liters Air Volume	ug MITC Taken	% Recovery
58	3	7	40 - 48	0.5	88* (87 - 88)**
70	3	7	47 - 53	0.5	74 (71 - 79)
81	4	7	38 - 44	0.5	43 (32 - 57)
81	2	4	25	0.5	66 (59 - 72)
92	3	7	41 - 42	0.5	53 (41 - 63)
92	2	4	22 - 25	0.5	72 (70 - 75)
58	3	7	36 - 44	5	98 (92 - 104)
70	3	7	40 - 43	5	87 (82 - 92)
81	5	7	34 - 57	5	50 (44 - 58)
81	2	4	21 - 24	5	69 (66 - 72)
92	3	7	37 - 42	5	55 (48 - 62)
92	3	4	20 - 26	5	83 (78 - 89)
58	3	7	43 - 47	25.5	103 (101 - 107)
70	3	7	42 - 49	25.5	98 (91 - 99)
81	1	6	35	25.5	78
92	3	7	39 - 41	25.5	77 (73 - 82)
92	1	4	26	25.5	76
58	2	6	37 - 38	51.5	93 (91 - 94)
70	4	7	38 - 46	51.5	98 (94 - 104)
81	1	6	36	51.5	97
81	1	6	39	227.4	80
92	1	6	36	51.5	100
92	1	7	42	102.9	100
92	1	7	41	227.4	83

NOTES: * = Mean
** = Range
% Recovery not corrected for desorption efficiency (D.E.)

Table 6. Recovery Data for MITC in Air at High (>81%) Relative Humidity with the Use of Silica Gel as a Pre-trap for Moisture

Sampling Flow Rate = 0.1 L/min.

% R.H.	Hours Sampling Time	Liters Air Volume	ug MITC Taken	ug MITC Found	% Recovery
81	6	36	0.5	0.40	79
81	7	42	0.5	0.37	74
81	7	41	5	4.43	89
81	7	46	5	4.35	87
92	6	38	0.5	0.38	75
92	7	45	0.5	0.36	71
92	7	44	5	4.39	88
92	7	44	5	4.21	84
92	7	46	25	22.9	92
92	7	45	25	22.7	91
92	7	46	59	55.9	95
92	7	40	59	51.9	88

NOTE: % Recovery not corrected for desorption efficiency (D.E.)

APPENDIX IV.

QA/QC AUDIT REPORT

STATE OF CALIFORNIA PETE WILSON, Governor

AIR RESOURCES BOARD
2020 L STREET
P.O. BOX 2815
SACRAMENTO, CA 95812

MEMORANDUM

TO: George Lew, Chief
Engineering Evaluation Branch

THROUGH: Jeff Cook, Chief
Quality Management and Operations Support Branch

FROM: Alice Westerinen, Manager Alice
Quality Assurance Section

DATE: January 28, 1994

SUBJECT: Methyl Isothiocyanate Monitoring Audit Report

Please find attached the final quality assurance audit report on the Methyl Isothiocyanate monitoring project conducted in July and August of 1993 by the Engineering Evaluation Branch of the Air Resources Board, and the Environmental Health Laboratory of the Department of Health Services. The report consists of three parts: the results of a flow rate audit of the air samplers, the results of a system audit, and the results of an analytical performance audit.

If you have any questions, please contact Gabriel Ruiz of my staff at (916) 327-0085 or ATSS 467-0885.

Attachment

cc: Don Fitzell
Gabriel Ruiz

AUDIT REPORT

METHYL ISOTHIOCYANATE MONITORING IN KERN COUNTY

January 28, 1994

SUMMARY

In July and August of 1993, the Engineering Evaluation Branch of the California Air Resources Board conducted a study to document the ambient air concentrations of methyl isothiocyanate (MITC) in populated areas of Kern County during the period of peak use, and the airborne emissions in the vicinity of a treated field during and after an application of the pesticide. Ambient air was drawn at measured rates through glass sampling tubes containing adsorbant charcoal, and the samples were analyzed by the Environmental Health Laboratory (EHL) of the California Department of Health Services using a gas chromatography (GC) method.

On July 13, staff of the Quality Assurance Section of the Air Resources Board conducted flow rate audits of the air samplers used in the study. The audits were conducted with a mass flow meter traceable to the National Institute of Standards and Technology. The difference between the reported and the true flow rates averaged 0.3% with a range of -4.5% to 3.2% for the samplers used in the ambient monitoring, and -1.0% with a range of -7.8% to 3.9% for the samplers used in the application monitoring.

A system audit was conducted to review the sample handling and storage procedures, analytical methodology, and method validation. It was found that these were consistent with good laboratory practice. The only quality assurance deficiency noticed in the study was the lack of control charts. However, the laboratory used a test solution periodically to monitor the stability of the GC detector.

In October of 1992, eight samples spiked with measured amounts of MITC were submitted to the laboratory for analysis. The samples were prepared from crystalline MITC of 97% purity, which EHL obtained from Aldrich Chemical Company. The difference between the assigned and the reported MITC mass averaged 25.6%, and ranged from 7.8% to 36.9%. Also, seven samples were submitted to the Department of Pesticide Regulation, which was conducting a parallel study. The difference between the assigned and the reported MITC mass averaged 10.2%, and ranged from 4.9% to 22.5%.

A second performance audit of the EHL was conducted in August of 1993, using a 79% pure MITC sample obtained from Chem Service. The difference between the assigned and the reported MITC mass averaged 12.1%, and ranged from 2.2% to 16.9%.

AUDIT REPORT

METHYL ISOTHIOCYANATE MONITORING IN KERN COUNTY

INTRODUCTION

In July and August of 1993, the Engineering Evaluation Branch (EEB) of the California Air Resources Board (CARB) conducted a study to document the ambient air concentrations of methyl isothiocyanate (MITC) in populated areas of Kern County during the period of peak use, and the airborne emissions in the vicinity of a treated field during and after an application of the pesticide. Ambient air was drawn at measured rates through glass sampling tubes containing adsorbant charcoal, and the samples were analyzed by the Environmental Health Laboratory (EHL) of the California Department of Health Services.

Ken Bowers of the CARB's Quality Assurance (QA) Section conducted a flow rate audit of the samplers, and Gabriel Ruiz conducted a system audit of the field and laboratory operations and a performance audit of the analytical method.

FLOW RATE AUDIT

The air samplers consisted of two sampling tubes, each connected with Teflon tubing to a rotameter, which in turn was connected to an air pump. The sampling assembly was supported by a two meter section of galvanized steel tube (Figure 1). EEB staff calibrated the samplers by setting the flow rates so that the rotameters read 2.0 liters per minute (L/min), and then measuring the actual flow with a bubble meter. The average of the measured flow rates was then reported as the sample collection flow rate.

Four samplers used in the ambient monitoring and four used in the application monitoring were audited at the EEB's shop in Sacramento on July 13, 1993, before monitoring was initiated. The audits were conducted with a 3 L/min Matheson mass flow meter traceable to the National Institute of Standards and Technology (NIST), following the procedures outlined in Attachment I. The difference between the reported and the true flow rates averaged 0.3% with a range of -4.5% to 3.2% for the samplers used in the ambient monitoring (Table 1), and -1.0% with a range of -7.8% to 3.9% for the samplers used in the application monitoring (Table 2).

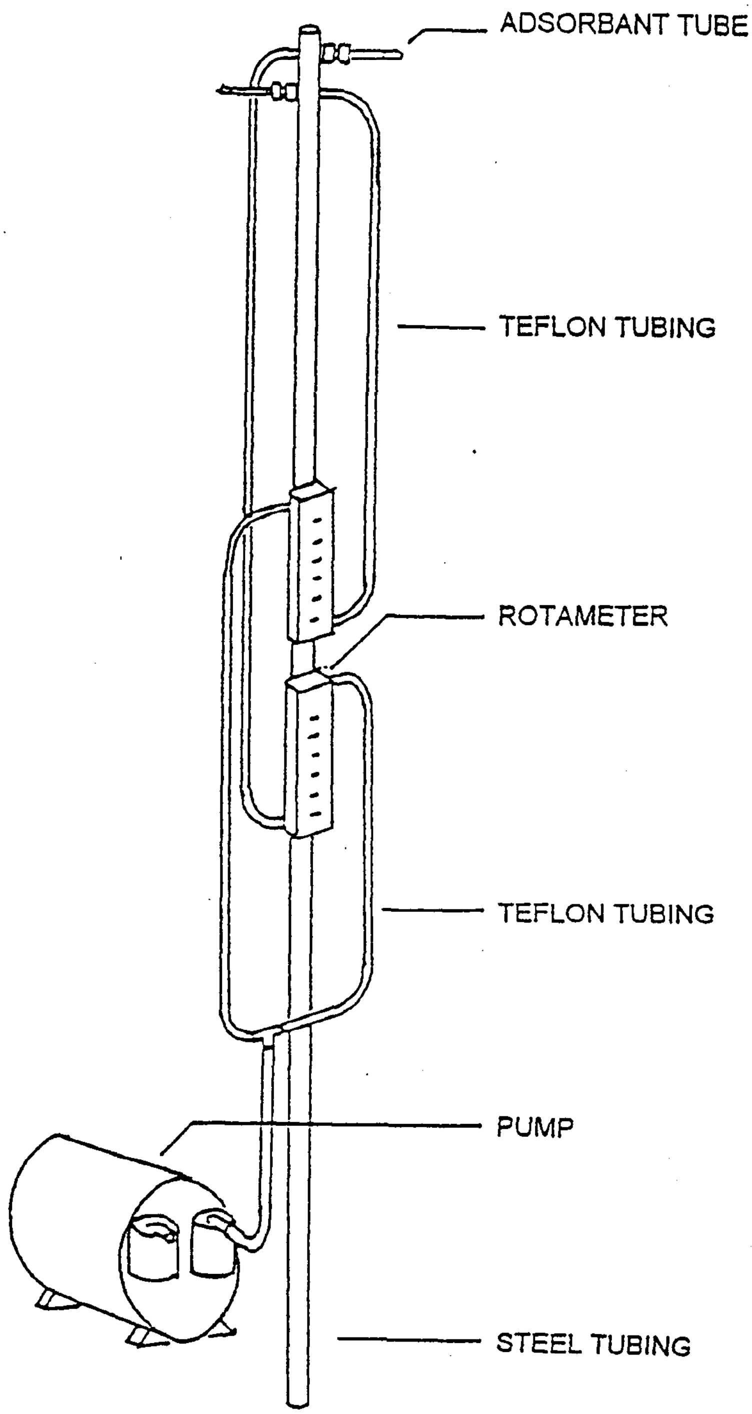


Figure 1. Air sampler used in the monitoring of MITC.

Table 1. Results of the flow rate audit of the air samplers used in the ambient monitoring of MITC.

Sampler Number	Rotameter Number	Reported Flow (L/min)	True Flow (L/min)	Percent Difference
5	5A	1.91	1.85	3.2
	5B	1.91	1.96	-2.6
6	6A	1.91	2.00	-4.5
	6B	1.91	1.86	2.7
7	7A	1.91	1.87	2.1
	7B	1.91	1.91	0.0
8	8A	1.91	1.90	0.5
	8B	1.91	1.89	1.1

Table 2. Results of the flow rate audit of the air samplers used in the application monitoring of MITC.

Sampler Number	Rotameter Number	Reported Flow (L/min)	True Flow (L/min)	Percent Difference
1	1A	1.88	1.91	-1.6
	1B	1.88	1.89	-0.5
4	4A	1.88	1.89	-0.5
	4B	1.88	1.84	2.2
19	19A	1.88	1.93	-2.6
	19B	1.88	2.04	-7.8
21	21A	1.88	1.88	0.0
	21B	1.88	1.81	3.9

$$\text{Percent Difference} = \frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

SYSTEM AUDIT

A system audit of the field and laboratory operations was initiated on August 11, 1993, to confirm that good laboratory practices were followed in the handling and storage of samples, analytical methodology, and method validation. The audit was conducted through a questionnaire sent to Sue Twiss of the EHL, and followed up by telephone conversations. The following is a discussion of the audit findings.

Sample Handling and Storage

Sampling was conducted by EEB staff, following the schedule specified in the sampling protocol. After sampling, the exposed charcoal tubes were collected, capped, and placed in screw-cap culture tubes. The culture tubes were then stored over dry ice in an ice chest until they were delivered to the laboratory on Friday of each week. Upon receipt at the laboratory, the samples were stored in a freezer at less than 0 ^oC. Extraction and analyses were carried out within two weeks of receipt.

Sample Analysis

The analytical method was adapted from ICI/Stauffer Chemical Company's method RRC-8235, "Methyl Isothiocyanate from Metham-Sodium Determination in Air". The method entails extraction of the exposed charcoal tubes with carbon disulfide and analysis by gas chromatography (GC).

Quality control activities performed to monitor and document the quality of the data included daily preparation of calibration standards and a five-point calibration; duplicate analyses of all the samples; analysis of two control samples, one laboratory spike and one laboratory blank per analytical run; one field spike and one field blank per shipment of samples; and one duplicate sample per sampling day. In addition, the samples were analyzed by a second laboratory and confirmed by mass spectroscopy at EHL, and the stability of the GC detector was monitored by injecting a test solution at least every two months. The only deficiency noticed was the lack of control charts.

Method Validation

The limit of detection was determined as 10 ng/mL using a one-sided t-test of the standard deviation of seven replicate injections at the 99% confidence interval. The method recovery (desorption efficiency) was determined as 76%.

Sample stability studies were conducted by spiking four sets of ten tubes each with 0.5, 5, 21-25, and 51 ug of MITC and storing them in a refrigerator. Four samples of each set were analyzed after 1 day, and the recoveries averaged 86%, 94%, 93% and 101%, respectively. Two samples of each set were analyzed after 7 days, and the recoveries averaged 78%, 101%, 96%, and 93%, respectively. The rest of the samples were analyzed after 14 days, and the recoveries averaged 76%, 85%, 83%, and 94%, respectively.

Documentation

Each sample was given a unique sample number in the field. Upon receipt at the laboratory, each sample was given a new number which consisted of the batch number plus the sample's field number. All the samples received at the laboratory were accompanied by chain-of-custody records. The field data sheets containing the sample collection information were retained by the EEB staff. The information included sampler location, date, start and stop times, initial and final flow rates, and comments about unusual conditions.

Bound notebooks with numbered pages were kept as laboratory books and instrument logs. The entries made in the laboratory book included project identification, sample number, sample type, date of receipt, date of analysis, results of the analysis, and analyst. Hard copies of the chain-of-custody records, and chromatograms are saved in an accessible form for at least five years or until any litigation is final.

LABORATORY PERFORMANCE AUDIT

In October of 1992, eight audit samples spiked with measured amounts of MITC were submitted for analysis to the EHL to evaluate the accuracy of the analytical method. The samples were prepared on October 5, following the procedures outlined in Attachment II, from crystalline MITC of 97% purity, which EHL obtained from Aldrich Chemical Company, and were extracted and analyzed within two weeks of preparation. In addition, a duplicate set of samples was submitted to the Department of Pesticide Regulation (DPR), which was conducting a parallel study, and another set was stored in a freezer for confirmation purposes.

The difference between the assigned MITC mass and the EHL's reported values showed a positive bias averaging 25.6%, and ranging from 7.8% to 36.9% (Table 3). Similarly, the difference between the assigned mass and the DPR's reported values showed a positive bias averaging 10.2% and ranging from 4.9% to 22.5% (Table 4). It was speculated that the source of the bias was a dilution error in the preparation of the audit samples, since both laboratories had method recovery rates lower than 100%. Furthermore, a chromatographic comparison showed the results of several solutions prepared from the spiking solution to be 42% higher than those of two sets of similar solutions prepared by the EHL's analysts. On November 3, 1992, the EHL analyzed four of the samples stored in the freezer, but the results were inconclusive because the MITC had deteriorated significantly. The difference between the assigned mass and the reported values averaged -25.7% and ranged from -25.9% to -19.6% (Table 5).

A second performance audit of the EHL was conducted in August of 1993, using a 79% pure MITC sample obtained from Chem Service, and paying extra attention to the preparation of the audit samples. However, the results again showed a positive bias averaging 12.1% and ranging from 2.2% to 16.9% (Table 6).

Table 3. Results of EHL's October 1992 analytical performance audit.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
MITC-1	2.55	3.49	36.9
MITC-2	0	ND	NA
MITC-3	0.51	0.63	23.5
MITC-4	1.02	1.20	17.6
MITC-5	2.55	3.00	17.6
MITC-6	0	ND	NA
MITC-7	1.02	1.38	35.3
MITC-8	0.51	0.55	7.8

$$\text{Percent Difference} = \frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

Table 4. Results of DPR's October 1992 analytical performance audit.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
MITC-21	0	ND	NA
MITC-22	2.55	2.84	11.4
MITC-23	0.51	0.58	13.7
MITC-24	1.02	1.25	22.5
MITC-25	1.02	1.07	4.9
MITC-26	2.55	2.69	5.5
MITC-27	0.51	0.56	9.8

Table 5. Results of EHL's November 1992 analyses of the audit samples stored in a freezer.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
MITC-28	0	ND	NA
MITC-29	0.51	0.41	-19.6
MITC-30	1.02	0.73	-28.4
MITC-31	2.55	1.89	-25.9

Table 6. Results of EHL's August 1993 analytical performance audit.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
MITC-36	1.36	1.47	8.1
MITC-37	0.45	0.51	13.3
MITC-38	2.27	2.58	13.7
MITC-39	1.36	1.59	16.9
MITC-40	0	ND	NA
MITC-41	2.27	2.54	11.9
MITC-42	0.45	0.46	2.2

$$\text{Percent Difference} = \frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

CONCLUSIONS

In general, good quality control practices were observed during the study. The records for field operations were appropriate; the flow rates reported were in good agreement with the actual flow rates measured by the QA staff; the sample handling and storage procedures, the analytical methodology, and the method validation were consistent with good laboratory practices; and the results of the analytical performance audit were in fair agreement with the expected values.

The only quality assurance deficiency noticed was the lack of control charts. Control charts would have documented that the method was in statistical control at the time of the analyses; however, the laboratory monitored the stability of the detector regularly.

Flow Audit Procedure for Air Samplers Used in Pesticide Monitoring

Introduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST traceable Brooks automatic flow calibrator. The audit device is connected in series with the sampler's flow meter, and the flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's corrected flow is then compared to the true flow, and a percent difference is determined.

Equipment

The basic equipment required for the air sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST-traceable mass flow meter.
2. Calibrated differential pressure gauge with laminar flow element.
3. 1/4" O.D. Teflon tubing.
4. 1/4", stainless steel, Swagelock fittings.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 V AC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.
2. Connect the inlet port of the audit device to the outlet port of the sampler's flow control valve with a 5 ft. section of Teflon tubing and Swagelock fittings.
3. Connect the outlet port of the audit device to the pump with another 5 ft. section of Teflon tubing and Swagelock fittings.
4. Allow the flow to stabilize for at least 1-2 minutes and record the flow rate indicated by the sampler and the audit device's response.
5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the corrected measured flow rate.

Performance Audit Procedure
for the Laboratory Analysis of MITC

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory measuring the ambient concentrations of MITC. The audit is conducted by submitting audit samples spiked with known concentrations of MITC. The analytical laboratory reports the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. MITC, 97% pure (obtained from EHL), and 79% pure (obtained from Chem Service)

2. Toluene, High Purity, B&J Lot #AO 512

3. Charcoal Adsorbant Tubes, 600 mg, SKC Lot #120

4. Microsyringe, 25 uL

Safety Precautions

Prior to handling any chemical, read the manufacturer's Material Safety Data Sheets (MSDS). Avoid direct physical contact with chemicals. Avoid breathing vapors. Use only under a fume hood. Wear rubber gloves, safety glasses, and protective clothing.

Sample Preparation

10 mg/mL MITC Stock Solution: Weigh 100 mg of MITC into a clean 10 mL volumetric flask. Record the actual MITC weight. Dissolve with toluene and dilute to the mark. Record the concentration.

0.1 mg/mL MITC Spiking Solution: Transfer 100 uL of the MITC stock solution into a clean 10 mL volumetric flask and dilute with toluene to the mark. Record the concentration.

Prepare the audit samples from the 0.1 mg/mL MITC spiking solution and pure toluene according to the following table:

Sample	0.1 mg/mL MITC Vol (uL)	Toluene Vol (uL)	Sample	0.1 mg/mL MITC Vol (uL)	Toluene Vol (uL)
MITC-1	25.0	0.0	MITC-28	0.0	25.0
MITC-2	0.0	25.0	MITC-29	5.0	20.0
MITC-3	5.0	20.0	MITC-30	10.0	15.0
MITC-4	10.0	15.0	MITC-31	25.0	0.0
MITC-5	25.0	0.0	MITC-32	0.0	25.0
MITC-6	0.0	25.0	MITC-33	5.0	20.0
MITC-7	10.0	15.0	MITC-34	10.0	15.0
MITC-8	5.0	20.0	MITC-35	25.0	0.0
MITC-21	0.0	25.0	MITC-36	15.0	0.0
MITC-22	25.0	0.0	MITC-37	5.0	0.0
MITC-23	5.0	20.0	MITC-38	25.0	0.0
MITC-24	10.0	15.0	MITC-39	15.0	0.0
MITC-25	10.0	15.0	MITC-40	0.0	0.0
MITC-26	25.0	0.0	MITC-41	25.0	0.0
MITC-27	5.0	20.0	MITC-42	5.0	0.0

1. Label the tubes, and break off both ends of each tube.

2. Remove the adsorbant charcoal from the secondary section.

3. Use a microsyringe to transfer the appropriate volumes of the spiking solution and toluene into the adsorbant bed of the primary section of the tube. Do not allow the solution to run down the sides of the tube.

4. Cap both ends of the tubes with the plastic caps provided and store them in a freezer until ready for analysis.

APPENDIX V

LABORATORY REPORTS

EHLB Laboratory Report

MITC AMBIENT RESULTS BY DATE OF ANALYSIS

DATE	SAMPLE NAME	MITC CONCENTRATION (ug/tube) FRONT	BACK	TOTAL
28 JULY 93	1R	1.11	<LOD	1.11
	1-BF	1.16	<LOD	1.16
	1-S1	0.667	<LOD	0.667
	1-M	2.56	<LOD	2.56
	1-V		<LOD	
29 JULY 93	1-V	6.42		6.42
	2-R	<LOD	<LOD	<LOD
	2-BF	0.815	<LOD	0.815
	2-S1	0.686	<LOD	0.686
	2-M	2.85	<LOD	2.85
	2-V		<LOD	
29-30 JULY 93	3-R		<LOD	
	3-BF		<LOD	
	3-S1	0.685	<LOD	0.685
	3-M		<LOD	
	3-V		<LOD	
30-31 JULY 93	2-V	5.35		5.35
	3-R	5.62		5.62
	3-BF	15.2		15.2
	3-M	26.4		26.4
	3-V	32.0		32.0
	4-R	0.075	<LOD	0.075
	4-BF		<LOD	
	4-S1	0.657	<LOD	0.657
	4-M		<LOD	
	4-V		<LOD	
	4-C	0.745	<LOD	0.745
	4-BLK	<LOD	<LOD	<LOD
2 AUG 93	4-BF	15.7		15.7
	4-M	43.1		43.1
	4-V	47.7		47.7
4-5 AUG 93	5-R	<LOD	<LOD	<LOD
	5-BF		<LOD	
	5-S1		<LOD	
	5-M		<LOQ	
	5-V		<LOQ	
	6-R	<LOD	<LOD	<LOD
	6-BF		<LOD	
	6-S1		<LOD	
	6-M		<LOD	
	6-V		<LOD	
	6-B	<LOD	<LOD	<LOD

MITC AMBIENT RESULTS BY DATE OF ANALYSIS

DATE	SAMPLE NAME	MITC CONCENTRATION (ug/tube) FRONT	BACK	TOTAL
5-6 AUG 93	5-BF	5.96		5.96
	5-S1	0.815		0.815
	5-M	20.3		20.3
	5-V	27.9		27.9
	6-BF	2.39		2.39
	6-S1	0.601		0.601
	6-M	14.9		14.9
	7-R	<LOD	<LOD	<LOD
	7-BF	0.895	<LOD	0.895
	7-S1	0.548	<LOD	0.548
	7-M	1.11	<LOD	1.11
	7-V	7.91	<LOD	7.91
	8-R	0.182	<LOD	0.182
	8-BF	3.03	<LOD	3.03
	8-S1	0.549	<LOD	0.549
	8-M	11.6	<LOD	11.6
	8-V	21.8	<LOD	21.8
	8-B	<LOD	<LOD	<LOD
	8-C	0.565	<LOD	0.565
11-12 AUG 93	DUP.5-V		0.104	
13-14 AUG 93	DUP.5-V	38.8		38.9
16-17 AUG 93	6-V	26.1		26.1
17-18 AUG 93	DUP.6-M	16.4	<LOD	16.4
	DUP.8-BF	4.06	<LOD	4.06

CDFA laboratory Report

March 15, 1994

To: Catherine Cooper

From: Jorge L. Hernandez

Subject: MITC MDL

MITC air samples are prepared on 5 mL final volume. Samples' 1BF, 2BF, B, 2M, 4R, 4V, 1V were run twice. The first time using the standard curve (0.25ng/µL to 10 ng/µL) recommended by the validate method. This curve gave an MDL of 1.0ng/sample. The second time the standard curve was 0.04, 0.1, and 0.2ng/µL. This second standard curve gives an MDL of 0.2 ug/sample. Samples' 1BF and 2BF were also run on the MSD using the higher standard curve.

The two samples, 1BF and 2BF that were below than the declared MDL of 1.0 ng/sample, are clearly present on the GC with a TSD. However, they can not be confirmed by MSD because of sensitivity problem.

I am also attaching a copy of the results reported for this set of samples.

These samples were analyzed on October 20, 1993.

The results for the split MITC samples with Air Resources Board are:

Sample #	CDFA Lab #	Sample Results (ug)			TSD MDL (ug/sample)	MSD MDL (ug/sample)
		Front	Back	Glass wool		
1BF	0684	0.59	ND	ND	0.2	1.0
2BF	0685	0.48	ND	ND	0.2	1.0
B	0686	ND	ND	ND	0.2	1.0
2M	0687	1.77	ND	ND	0.2	1.0
4R	0688	ND	ND	ND	0.2	1.0
4V	0689	45.39	ND	ND	0.2	1.0
1V	0690	4.03	ND	ND	0.2	1.0
Blank	0771	ND	ND	ND	0.2	1.0
5ug Spike	0772	4.30	ND	ND	0.2	1.0